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Polyglycerol-Polycaprolactone-Polycitric acid Copolymer and Its Self-Assembly to Produce Medium-Responsive Nanoparticles

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Calculation of Molecular weight of Ad-PG using ^{1}H NMR data

Ratio of protons of a glycidol unit after opening against its hydroxyl protons is: 5/2 = 2.5
This ratio for 10 unit attached to adenine core will be 50/12 = 4.1 (peak area of water of DMSO is diminished from peak area of PG hydroxyl groups; 1- 0.2 = 0.8).
Therefore 10 × 74 = 740 + 133 (adenine) = 873

Calculation of the number of arms of Ad-PG-PCL and also their length or molecular weights using ^{1}H NMR data

The peak area ratio of signal of end methylene groups of PCL chains to the protons of aromatic rings of adenine and that to the methylene groups of PCL backbone was used to calculate the number of arms of Ad-PG-PCL and also their length or molecular weights respectively. Number of arms was also calculated by using the peak area ratio of PG methylene groups to all methylene groups of PCL chains:

Peak area for end methylene groups of PCL is around 0.1
Peak area for O-CH2- groups is 1
0.1 2
1 x = 20/2 = 10 number of units for each arm
10 × 114 = 1140 molecular weight for each arm

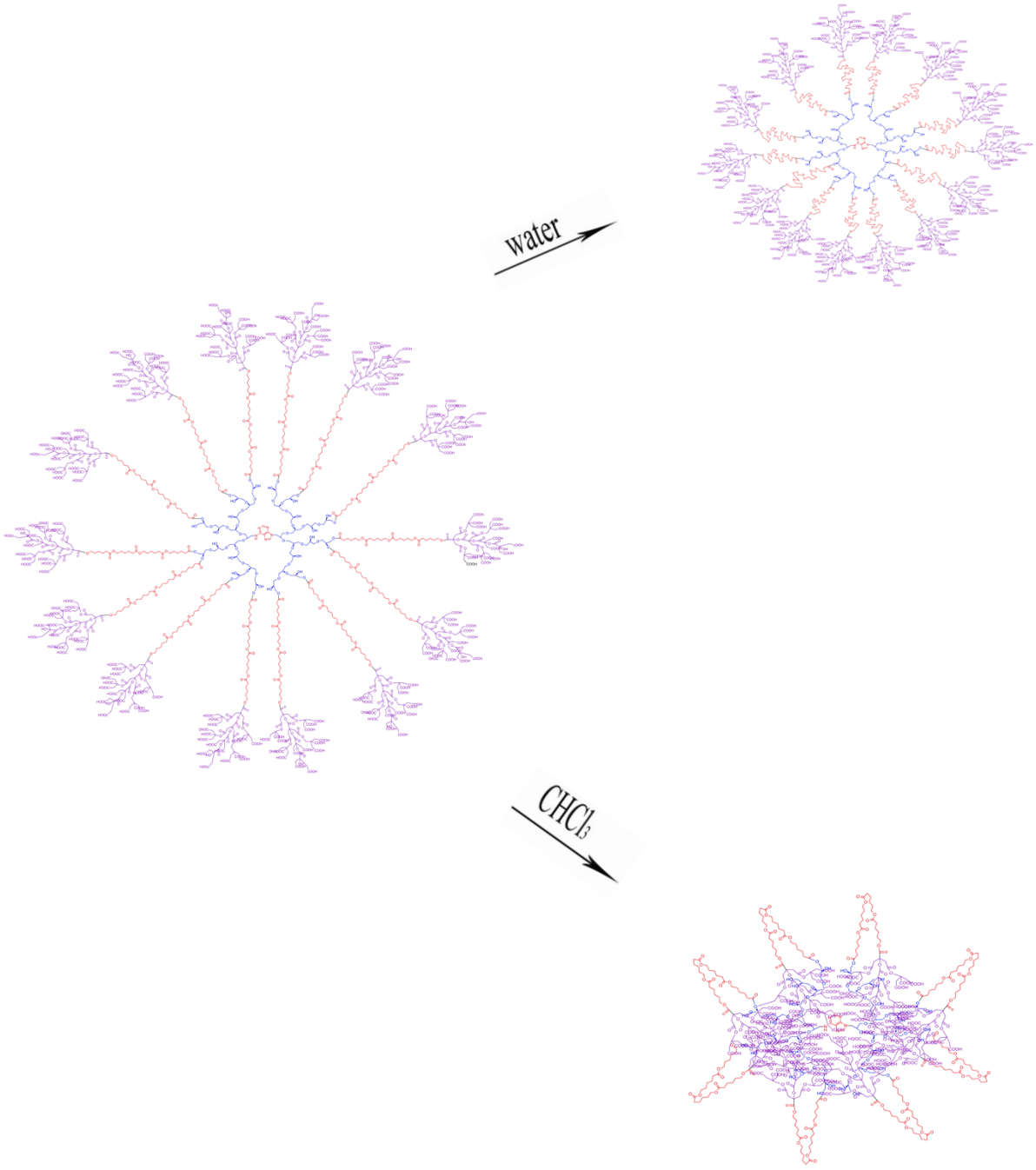
Peak area for methylene groups of PG divide to that for end methylene groups of PCL
= 1.5/0.1 = 15
This ratio could be obtained for 50/3.3 = 15
Peak area for the same region in Ad-PG spectra = 3.3 number of PCL arms
3.3 × 1140 = 3762 molecular weight for PCL block
3762 + 873 = 4635 molecular weight for Ad-PG-PCL

Calculation of Molecular weight of PCA block and also Ad-PG-PCL-PCA using ^{1}H NMR data

Peak area for –OCH2- (4 ppm) groups of PCL in Ad-PG-PCL-PCA = 1.4
Peak area for citric acid methylene groups = 2.7
10 × 3.3 × 2 = 66

1.4 66
2.7 x = 127 / 4 = 31.8 citric acid units × 192 = 6109 molecular weight of citric acid block

4635 + 6109 = 10744 molecular weight for Ad-PG-PCL-PCA



Scheme S1. Changes in the conformation of Ad-PG-PCL-PCA as a response to the solvent. In an organic solvent with the medium polarity such as chloroform which should be a good solvent for PCL block but nonsolvent for PG and PCA blocks, PCA block turn back onto the PG in the inner part of HLHA and both blocks cover by PCL loops. In water which is a good solvent for PCA and PG blocks and nonsolvent for PCL block, HLHA shrink to hide PCL in a PCA and PG cover.

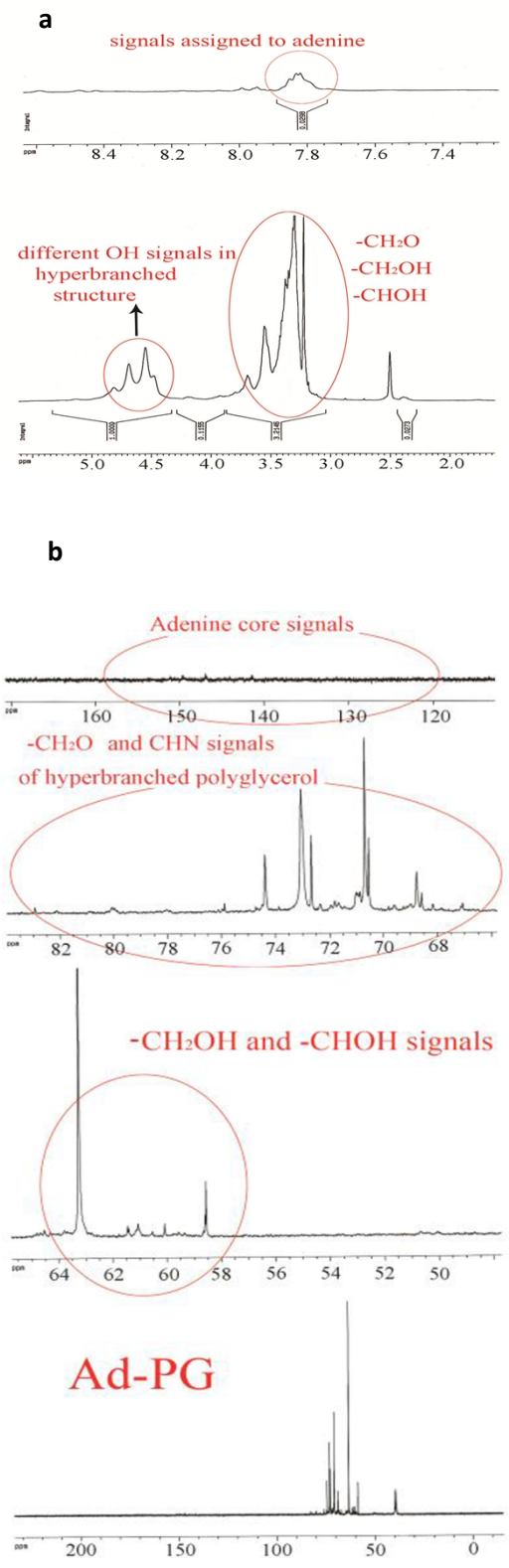


Figure S1. a) ^{1}H NMR spectra of Ad-PG in DMSO-d6 solvent. b**)** ^{13}C NMR spectra of Ad-PG in DMSO-d6 solvent

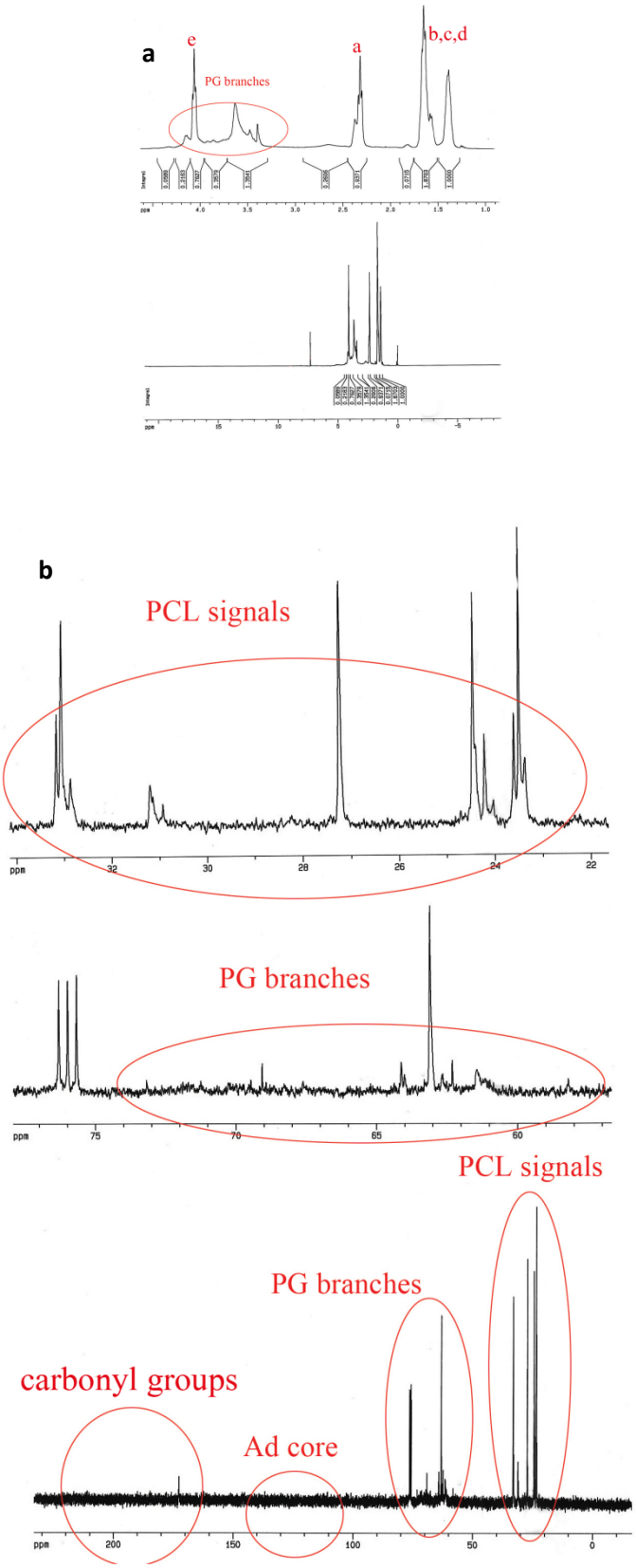


Figure S2. a) ^{1}H NMR spectra of Ad-PG-PCL in chloroform solvent. b) ^{13}C NMR spectra of Ad-PG-PCL in chloroform solvent

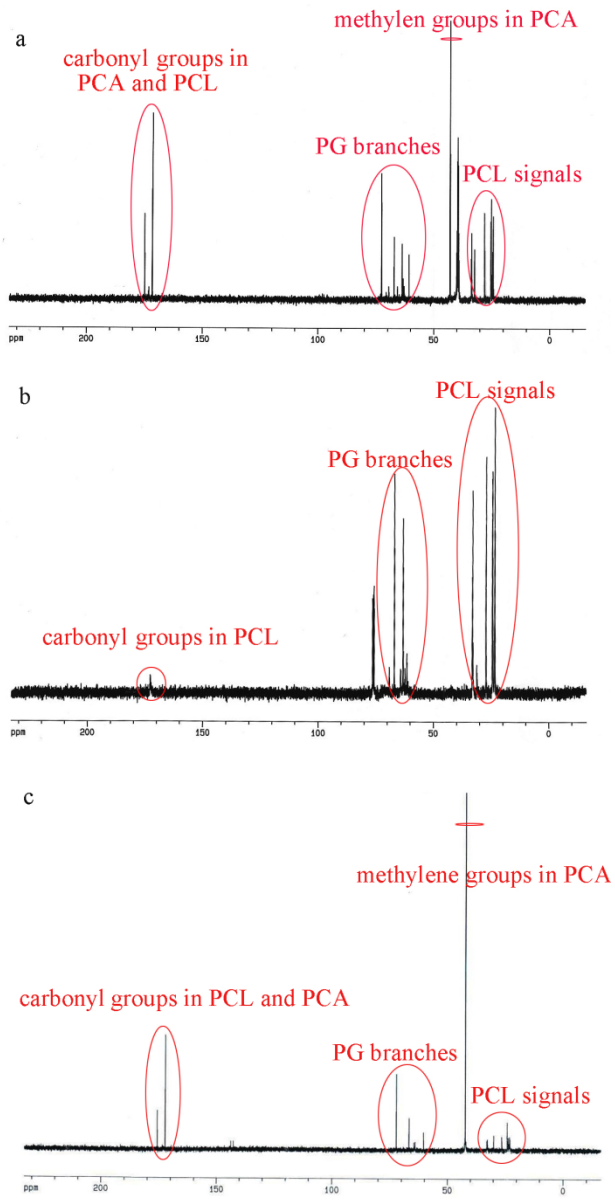
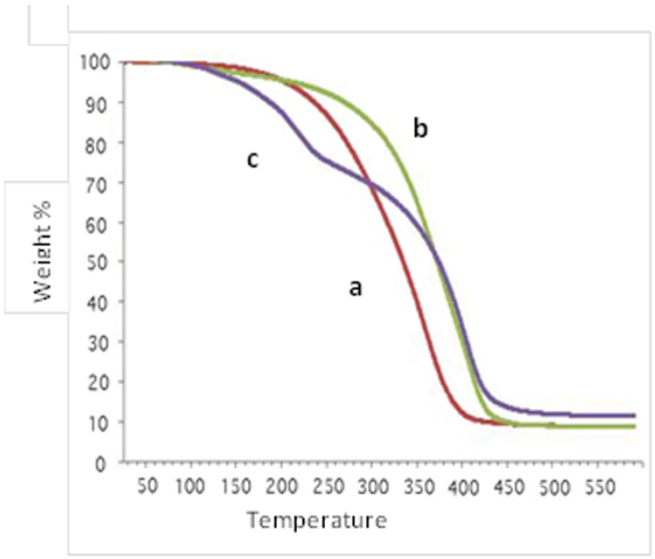
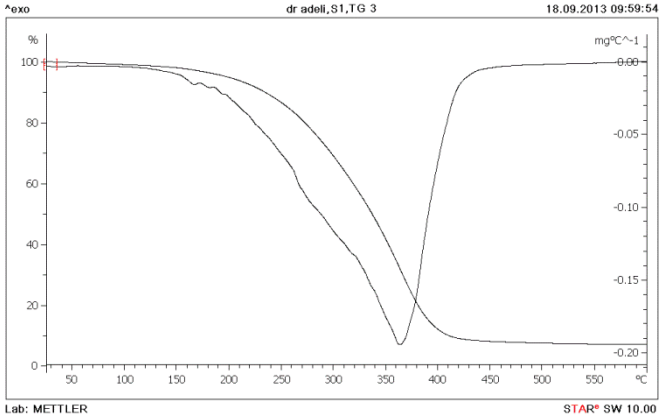


Figure S3. ^{13}C NMR spectra of Ad-PG-PCL-PCA in DMSO-d6, CDCl3 and D_2O. "a" is the ^{13}C NMR spectra of HLHA in DMSO-d6. "b" is the same spectra in chloroform and "c" is ^{13}C NMR spectra of the same compound in D_2O .


Weight %
Temperature
a
b
c


^exo
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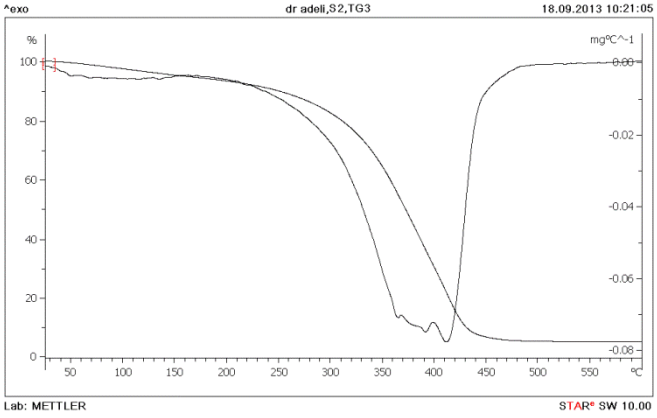
STAR° SW 10.00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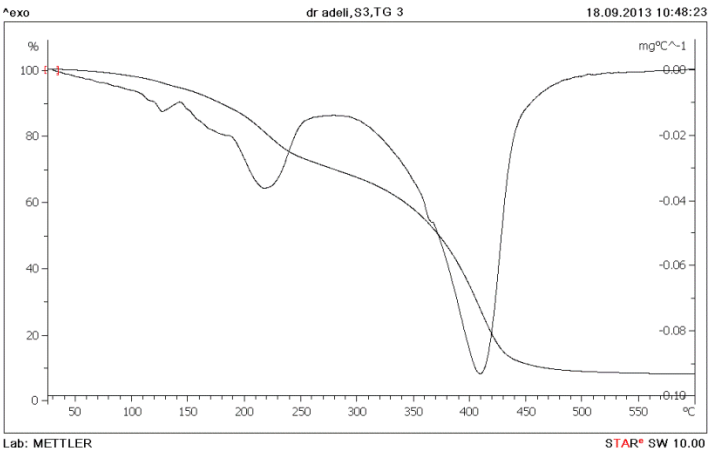
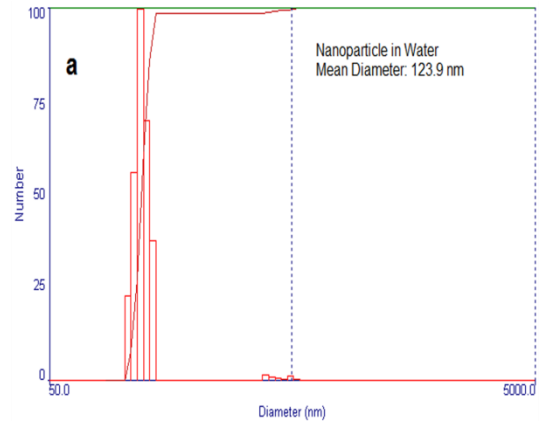
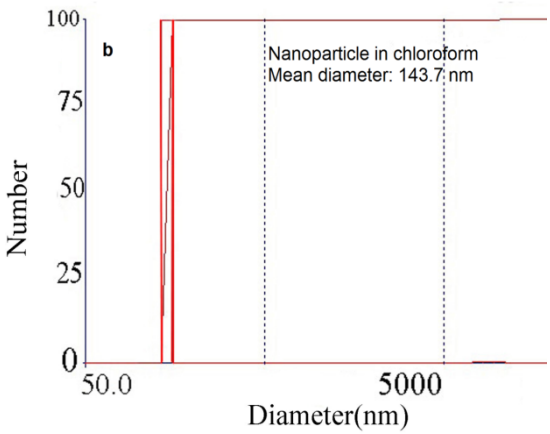


Figure S4. TGA diagrams of a) Ad-PG, b) Ad-PG-PCL, and c) Ad-PG-PCL-PCA. The same TGA diagrams with DTA curves can be see for Ad-PG, Ad-PG-PCL, and Ad-PG-PCL-PCA from top to dawn respectively.





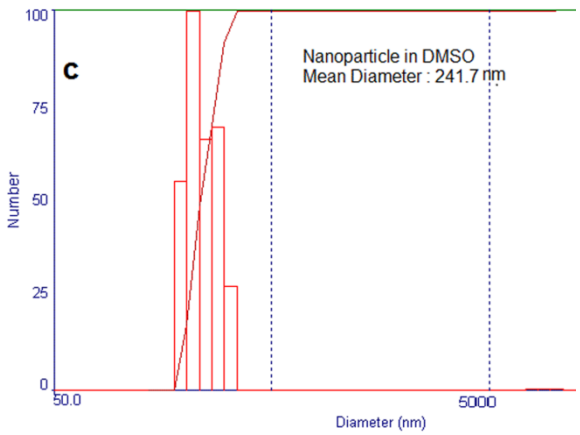


Figure S5. DLS diagrams for HLHA in a) water, b) chloroform and c) DMSO.

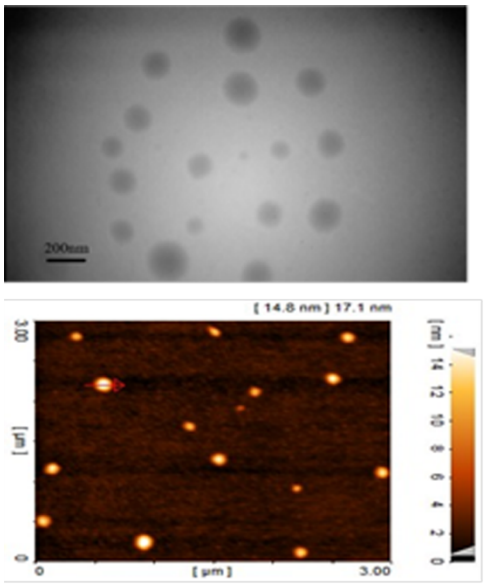


Figure S6. Topographic AFM images of a nanoparticle recorded in contact mode and by using a) 0.1, b) 0.2, c) 0.3, d) 1.5, and e) 2 nN forces. f) There is not considerable change in the height of nanoparticle upon increasing the force of the tip, confirming that nanoparticles are not hollow.

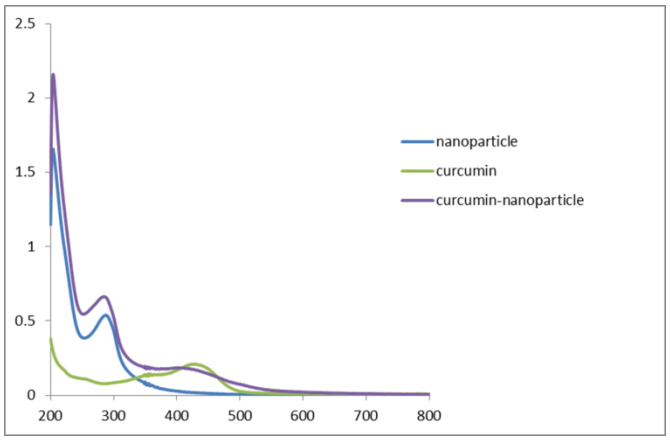
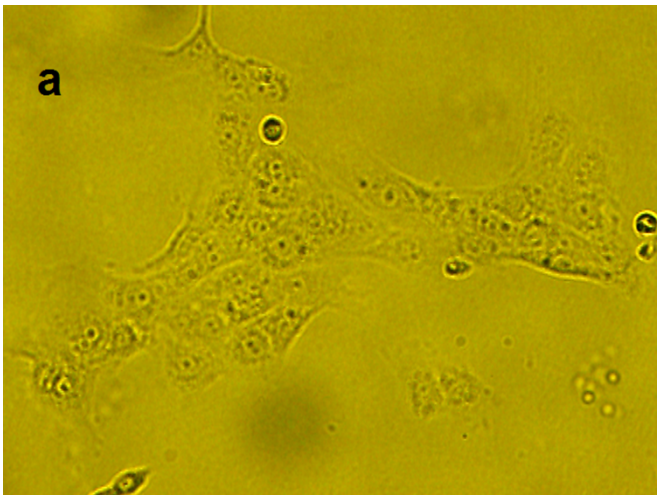


Figure S7. UV-vis spectra of nanoparticle and curcumin loaded in nanoparticles in water and free curcumin in methanol.



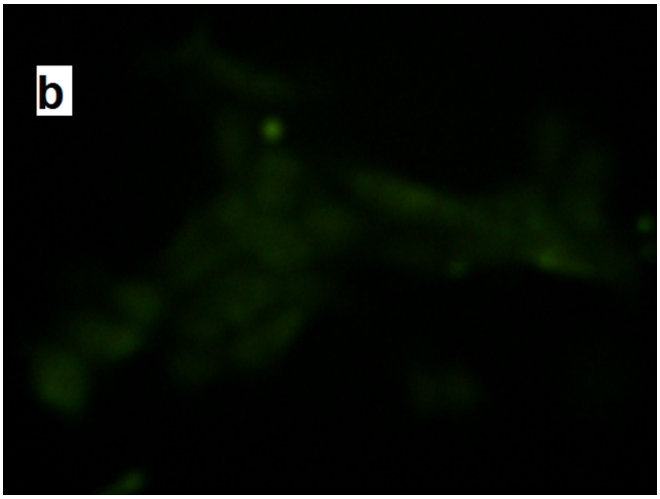


Figure S8. Bright-field image and Fluorescence image of 4T1 cells incubated with curcumin loaded nanoparticles (a and b) and nanoparticles as control cells (c and d).